

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
4 November 2004 (04.11.2004)

PCT

(10) International Publication Number
WO 2004/094341 A1

(51) International Patent Classification⁷: **C04B 41/89**
(21) International Application Number:
PCT/EP2004/004197
(22) International Filing Date: 21 April 2004 (21.04.2004)
(25) Filing Language: English
(26) Publication Language: English

(30) Priority Data:
M02003A000117 23 April 2003 (23.04.2003) IT

(71) Applicant (for all designated States except US): **CE-
RAMICHE GAMBARELLI S.R.L.** [IT/IT]; Strada
Statale 569, 224, I-41050 Solignano (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **GAMBARELLI,
Commendator, Ivana** [IT/IT]; Strada Statale 569, 224,
I-41100 Solignano (IT). **POZZI, Giuseppe** [IT/IT]; Strada
Statale 569, 224, I-41050 Solignano (IT).

(74) Agent: **GUARESCHI, Antonella**; Gidiemme S.R.L.,
474/M, Via Giardini, I-41100 Modena (IT).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Euro-
pean (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,
GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: A PROCEDURE FOR THE REALISATION OF CERAMIC MANUFACTURES, IN PARTICULAR, PORCELAIN
STONEWARE TILES AND TRIM PIECES, WITH ANTI POLLUTION AND ANTI-BACTERIAL PROPERTIES AND PROD-
UCTS THEREBY OBTAINED.

(57) Abstract: This invention falls into the field of ceramic manufactures, in particular tiles and trim pieces made of porcelain
stoneware. Titanium dioxide is applied to the glaze and to the layer covering the tiles so that a photocatalytic oxidation action can
be produced acting against the polluting and bacterial agents present in the atmosphere.



WO 2004/094341 A1

10/554167

JC09 Rec'd PCT/PTO 21 OCT 2005

DESCRIPTION

5 **A procedure for the realisation of ceramic manufactures, in particular, porcelain stoneware tiles and trim pieces, with anti pollution and anti-bacterial properties and products thereby obtained.**

Technical field

10 The invention relates to a procedure for the realisation of ceramic manufactures, in particular, porcelain stoneware, single-fired, monoporou or double-fired tiles and trims pieces with anti-pollution properties and products thereby obtained.

15 **Background Art**

For some time now, it has been common practice to produce manufactures with anti-bacterial and anti-pollution properties destined for the building industry with a wide range of applications such as, construction conglomerates, panelling for road networks and self-locking blocks for
20 paving.

These manufactures are constituted, substantially, of a cement-based conglomerate whose mass contains particles of titanium dioxide, TiO_2 , a property of which is its capacity to reduce the polluting agents present in the surrounding air.

25 Of these polluting agents, particular attention should be focussed on the polycyclic aromatic hydrocarbons (PAH) derived from the incomplete combustion of organic materials, wood, coal, oil, and its derivatives, and also the nitrogen oxides (NO_x) present in the exhaust fumes from heating systems, industrial plants, motor vehicles, industrial wastes and pesticides.

30 The abatement of the level of environmental NO_x reduces both the possibility of acid rain and the presence of nitrates which are harmful to humans and vegetation. The bacteria which can be attacked by the presence of TiO_2 include, for example, Staphylococci and Escheria Coli.

This result is due to the fact that the ultraviolet radiation of solar light,
35 together with the humidity, interacts with the titanium dioxide particles, leading to the production of active oxygen which effectively oxidises the

aforesaid polluting and bacterial agents present in the atmosphere.

The products of the aforesaid oxidation are removed by water, either rainwater or washing water, and also by the alkaline nature of the cement conglomerates which, until now, have been realised with photocatalytic properties. Moreover, the aforesaid removal and elimination of the polluting products prevent their stagnation on the surface of the said manufactures, ensuring the original colours and their attractive appearance are maintained over time.

The drawback of the commonly-known manufactures with photocatalytic properties lies in the cement base of the said products which cause the said manufactures to have a rough surface and, consequently, limited possibility of high quality aesthetic variants and, consequently, limited possibility of application in the field of external wall coverings for the building industry.

Much higher aesthetic quality, for external wall coverings, is offered by manufactures of a ceramic nature, in particular porcelain stoneware tiles or those made of other pastes, such as single-fired or monoporosa materials; however, until now, as far as the applicant is aware, no such material has been realised with polluting and antibacterial agent abatement properties. The main reason for this lies in the fact that the production of ceramic tiles requires firing treatments involving extremely high temperatures which, in the case of the porcelain stoneware manufactures, reach 1,200°C, unlike the production cycle of cement-based manufactures, which are produced by mixing and subsequent compaction, without requiring any thermal treatments.

It is known that when the TiO_2 in the form of Anatase reaches 900°C, it is transformed entirely into Rutile, which, it has been demonstrated through experimentation, to be less effective than Anatase in particularly critical pollution situations such as on roads with a great deal of traffic. Moreover, it has been observed that, in the production phase, the transformation of Anatase into Rutile gives the glaze on ceramic manufactures a yellowish colour.

The applicant's studies have concentrated on the way in which the TiO_2 can be made to coexist with the aforesaid extremely high temperatures without the decay of its photocatalytic properties, in addition to ensuring the photocatalytic effect of the ceramic tiles obtained in this way do not cause a decline in the high aesthetic quality of the said tiles.

The applicant's research and experiments have led to different

considerations that are analysed hereunder.

The total presence of TiO_2 in a finished tile (as a percentage thereof) which provides the best results varies within a range of 1-25% of the total weight of the applications (glazes, silk-screening, engobe, etc.). It should be highlighted that the photocatalytic reaction of the TiO_2 to the polluting and bacterial agents does not involve the consumption of the said TiO_2 , which means the efficacy of its action remains constant over time. It should also be noted that TiO_2 can be mixed with both the glaze and the engobe (a covering formed of a thin layer of atomised clay applied to the partially dried clay) and can also be applied with the silk-screening pastes.

The effectiveness of the oxidation exerted by the TiO_2 on the bacterial and polluting agents increases in the event that a photo-reflecting layer is applied, either beneath the layer of glaze covering the tile or with the said covering layer; for example, both white pigments and silica particles mixed with the glaze can be used; in this way, the rate at which the solar light penetrates the tiles is increased and this increases the photocatalytic effect exerted by the TiO_2 .

It is known that TiO_2 converts NO_x into nitrate ions which, upon oxidation, become Sodium and Calcium nitrates, which are not noxious, and which precipitate in the form of salts; the latter are removable by simply washing with water. From this came the idea that this washing action would be increased by an increase in the exposed surface, therefore the creation of micro channels on the surface of the tile would facilitate the action of the water (rain water or washing water) when removing the products of the oxidation caused by the pollutants.

In parallel, it was observed that the increase in the surface exposed to the light increases the photocatalytic effect of TiO_2 and therefore it appeared evident to the applicant that it was also necessary to create, on the surface of the tiles, a plurality of non-uniform, micro uneven areas with the dual aim of permitting the solar light to hit the tiles from any direction and permit the air to better fix the NO_x which is decomposed by the ultraviolet radiation of the daylight.

To permit an efficacious retaining action of the gas developed during the night, while awaiting the daylight, the need to provide the tiles with materials able to store the said gas was considered. To this end, experimentation showed that the materials that absorb well are Zeolite and Petalite mixed with the glaze, or Magalite added to the traditional clays of which the tile base is composed.

Disclosure of Invention

The aim of this invention is to identify a procedure capable of enabling the production of ceramic manufactures, in particular porcelain stoneware, single-fired, monoporos or double-fired tiles and trim pieces, with photocatalytic properties for the reduction of ambient pollution.

In particular, the procedure for the realisation of ceramic manufactures, in particular porcelain stoneware tiles and trim pieces, with anti-pollution properties, in question in this invention, is characterised by the fact that the said procedure, in combination with the production steps usual for the production of traditional ceramics, comprises the following phases:

- application of a variable percentage of TiO_2 to the manufactures' engobe;
- application of a variable percentage of TiO_2 to the covering glaze, the silk-screening pastes and the engobe;
- application, with the covering layer, of particles of material designed to increase the refraction of the solar light to which the manufactures are exposed;
- addition of substances designed to absorb NO_x to the covering layer and/or to the material of which the engobe is composed;
- creation of micro channels in the covering layer of the ceramic manufactures, said micro channels being designed to increase the permeability to water of the said manufactures;
- realisation of micro uneven areas in the aforesaid covering layer, said micro uneven areas being designed to increase the exchange surface between the single manufacture and the atmosphere;
- insufflation of air, on certain ramps of the kiln, during the traditional firing at 1200°C ; said insufflation being designed to produce an improvement in the photocatalytic effect of the TiO_2 .

These and other characteristics will better emerge in the description that follows of a preferred embodiment illustrated, purely in the form of a non-limiting example.

After a first thermal treatment of a traditional type at low temperatures, designed, substantially, to facilitate the evaporation of at least part of the humidity present in the unfired tiles, the procedure continues with the application of the engobe and a glaze in which there is substantially 25% TiO_2 , preferably in the form of Anatase; this application is carried out, preferably, by means of traditional methods (for example, a disk booth) or

by means of airbrushes without air with suitably modified nozzles.

There may be Magalite in the engobe.

There is silica sand mixed in with the glaze and, possibly, also white pigments. These materials may also be mixed in with the engobe.

- 5 The application of the TiO_2 with the covering layer of the tiles, for example the silk-screening layer, envisages a presence of a percentage of the said TiO_2 , limited to the materials constituting the said layer, which may vary, substantially, from 20% to 100%.

- 10 In the said glaze application phase, Zeolite and/or Petalite are added for the purpose of increasing the effect of the Magalite mixed in with the engobe.

Contemporaneously, and also in the aforesaid covering layer, micro channels and uneven areas are produced.

- 15 Finally, then, during the application of the covering layer, using silk-screening machines of a commonly known type, four operations are performed contemporaneously by means of the use of four synchronised silicon rollers, in the following order: a first roller creates the micro uneven areas on each tile base, a second roller applies the substance(s) designed to increase the absorption of NO_x , a third roller applies the material designed to increase the refraction and a fourth roller compacts
20 everything, redefines the micro uneven areas and produces the micro channels.

- At this point, the definitive firing takes place, the said firing being of the traditional type as regards the temperature, which, for porcelain stoneware ceramic material, reaches around $1,200^\circ\text{C}$, but in the procedure in question in this invention, envisages a modification consisting in an insufflation of air directly into the firing kiln; said insufflation involves the use of a system of shutters positioned directly above the kiln and operated by software which controls, at the same time, the oxidisation, the
25 quantity of CO_2 and the TiO_2 melting point.

As the last phase of the procedure in question in this invention, a re-firing of the tiles may be effected at approximately 600°C , subject to the application, to the tiles fired the first time, of a thin layer of crystalline containing TiO_2 .

- 35 Over the course of the description, explicit reference has also been made to porcelain stoneware ceramic tiles as the ceramic manufactures, but the procedure in question in this invention can quite evidently also be applied, advantageously, to ceramic tiles of a different type, for example single-

fired, monoporos, double-fired, clinker tiles etc.

Moreover, over the course of the description, explicit reference has been made to tiles, but it is evident that the procedure in question in this invention is applicable, advantageously, to any type of ceramic product regardless of the form and dimensions.

The applicant has proceeded with the production of three classes of porcelain stoneware tiles:

- a) a tile without any modifications to the traditional firing and with the presence of TiO_2 essentially in the form of Rutile;
- 10 b) a tile obtained with the modification of the firing phase by means of the insufflation of air, intervening during the transformation of Anatase into Rutile;
- c) a tile, as in the previous point, but with the addition of a layer of TiO_2 after firing is complete. Tests have also been carried out in which this last typology of tile undergoes a re-firing at 600°C with the aim of improving the fixing of the TiO_2 still further.

The three typologies of tiles just mentioned underwent efficiency tests which lead to the conclusion that 100m^2 of treated tiles, with particular reference to those in typology c), can clean a volume of air of approximately $15,000\text{m}^3$ during a sunny day.

There will now follow a list of the production characteristics of the five embodiments originating from the aforesaid three tile typologies.

A first porcelain stoneware manufacture was obtained with the following production characteristics:

- 25 - engobe with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- serigraphy using iron molybdate;
- calcic glaze with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- 30 - application of 100% TiO_2 by silk-screening.

A second porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25% TiO_2 applied by means of a disk booth;
- silk-screening using iron molybdate;
- 35 - zinc glaze with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- application of 100% TiO_2 by silk-screening.

A third porcelain stoneware manufacture was obtained with the following

production characteristics:

- engobe with 25% TiO_2 applied by means of a disk booth;
- silk-screening using iron molybdate;
- glossy alkaline silica-boron glaze with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- application of 100% TiO_2 by silk-screening.

A fourth porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- glossy silica-boron-zirconium glaze with 25% TiO_2 ;
- application of 100% TiO_2 by silk-screening.

A fifth porcelain stoneware manufacture was obtained with the following production characteristics:

- engobe with 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- application of 100% TiO_2 by means of an airbrush without air, functioning under high pressure;
- application of 100% TiO_2 by silk-screening.

The advantage of the procedure in question in this invention consists in the fact that it enables the realisation of ceramic manufactures for finishing in the building industry capable of developing a photocatalytic oxidising action against polluting and bacterial agents.

Claims

1. A procedure for the realisation of ceramic manufactures, in particular tiles and trim pieces, made of porcelain stoneware, with anti-pollution properties, characterised by the fact that the said procedure, in combination with the production steps usual for the production of traditional ceramics, comprises the following phases:
 - application of a variable percentage of TiO_2 with the covering glaze, the silk-screening pastes and the engobe;
 - application of a variable percentage of TiO_2 with the layer covering the said manufactures;
 - application, with the covering layer, of particles of material designed to increase the refraction of the solar light to which the manufactures are exposed.;
 - addition of substances designed to absorb NO_x to the covering layer and/or to the material of which the engobe is composed;
 - creation of micro channels in the thickness of the covering layer of the ceramic manufactures, said micro channels being designed to increase the permeability to water of the said manufactures;
 - realisation of micro uneven-areas in the thickness of the aforesaid covering layer, said micro uneven areas being designed to increase the exchange surface between the single manufacture and the atmosphere;
 - insufflation of air during the traditional firing at 1200°C ; said insufflation being designed to produce and improvement in the photocatalytic effect of the TiO_2 .
2. A procedure according to claim 1, characterised by the fact that the presence of the TiO_2 in the single manufacture may vary from 1% to 25%.
3. A procedure according to claims 1 and 2, characterised by the fact that the TiO_2 is used preferably in the form of Anatase.
4. A procedure according to claim 1, characterised by the fact that the materials designed to increase the refraction of the solar light to which the tiles are exposed are constituted, preferably, of white pigments and particles of silica; the said pigments and the said silica can both be applied to the same ceramic manufacture.
5. A procedure according to claim 1, characterised by the fact that the

application of the TiO_2 to the covering layer is preferably obtained by means of an airbrush without air, functioning under high pressure; the engobe can also be applied following traditional methods, for example, by means of a disk booth.

6. A procedure according to claims 1 and 4, characterised by the fact that the application of the materials designed to increase the refraction of the solar light to which the tiles are exposed is obtained by means of silk-screening machines designed to apply glaze by means of silicone rollers according to the thickness wanted.
7. A procedure according to claim 1, characterised by the fact that the substances designed to facilitate the absorption of the NO_x are, preferably, Magalite and Zeolite and/or Petalite; the said Magalite is mixed in with the engobe, while the Zeolite and/or Petalite are mixed in with the glaze.
8. A procedure according to claims 1 and 7, characterised by the fact that the application to the covering layer of the substances designed to absorb NO_x is obtained by means of silk-screening machines designed to apply the glaze by means of silicone rollers according to the thickness wanted.
9. A procedure according to claim 1, characterised by the fact that the micro uneven areas are obtained by means of the action of silk-screening machine in which a silicone roller applies a first layer to the tile base directly.
10. A procedure according to claim 1, characterised by the fact that the micro channels are obtained by means of the action of a silicon roller.
11. A procedure according to claims 1, 6, 8 and 9 characterised by the fact that the application to the glaze of materials designed to increase the refraction of solar light and of substances designed to absorb NO_x , and the creation, also in the covering layer, of micro channels and uneven areas are obtained simultaneously through the use of four synchronised silicon rollers in the following order: a first roller creates micro uneven areas on the base of every single manufacture, a second roller applies the substance designed to absorb NO_x , a third roller applies the material designed to increase refraction and a fourth roller compacts everything, redefines the micro uneven areas and produces the micro channels.
12. A ceramic manufacture made of porcelain stoneware, characterised by the fact that the said item contains TiO_2 in the form of Anatase and/or

Rutile, the said TiO_2 is designed to give the aforesaid manufacture photocatalytic properties acting against the polluting and bacterial agents present in the atmosphere.

13. A ceramic manufacture according to claim 12, characterised by the fact that the said item is obtained by means of traditional firing with the addition of TiO_2 in the form of Rutile only.
14. A ceramic manufacture according to claim 12, characterised by the fact that the said item is obtained by means of a modification of the firing phase to 1200°C .
15. A ceramic manufacture according to claims 12 and 14, characterised by the fact that the said item is obtained by means of a modification of the firing phase through insufflation of air which is followed by the application of a layer of TiO_2 once the firing is complete.
16. A ceramic manufacture according to claims 12 and 15, characterised by the fact that the said item undergoes re-firing.
17. A first ceramic manufacture according to claims 12 to 16, characterised by the fact that the said item was obtained by means of:
 - engobe with substantially 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
 - silk-screening using iron molybdate;
 - calcic glaze with substantially 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
 - application of 100% TiO_2 by silk-screening.
18. A second ceramic manufacture according to claims 12 - 16, characterised by the fact that the said item was obtained by means of:
 - engobe with substantially 25% TiO_2 applied by means of a disk booth;
 - silk-screening using iron molybdate;
 - zinc glaze with substantially 25% TiO_2 applied by means of an airbrush without air, functioning under high pressure;
 - application of 100% TiO_2 by silk-screening.
19. A third ceramic manufacture according to claims 12 - 16, characterised by the fact that the said item was obtained by means of:
 - engobe with substantially 25% TiO_2 applied by means of a disk booth;
 - silk-screening using iron molybdate;
 - glossy alkaline silica-boron glaze with substantially 25% TiO_2 applied by means of an airbrush without air, functioning under

high pressure;

- application of 100% TiO₂ by silk-screening.

20. A fourth ceramic manufacture according to claims 12 - 16, characterised by the fact that the said item was obtained by means of:

- engobe with substantially 25% TiO₂ applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- glossy silica-boron-zirconium glaze with substantially 25% TiO₂;
- application of 100% TiO₂ by silk-screening.

21. A fifth ceramic manufacture according to claims 12 - 16, characterised by the fact that the said item was obtained by means of:

- engobe with substantially 25% TiO₂ applied by means of an airbrush without air, functioning under high pressure;
- silk-screening using iron molybdate;
- application of 100% TiO₂ by means of an airbrush without air, functioning under high pressure;
- application of 100% TiO₂ by silk-screening.

INTERNATIONAL SEARCH REPORT

PCT/EP2004/004197

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C04B41/89

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 100 18 458 A (ERLUS BAUSTOFFWERKE) 18 October 2001 (2001-10-18) claims column 1, line 56 - line 58 column 2, line 14 - line 19	12, 13, 16-21
X	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) & JP 11 157966 A (TOTO LTD), 15 June 1999 (1999-06-15) abstract	12, 13, 16-21
X	US 6 103 363 A (BOIRE PHILIPPE ET AL) 15 August 2000 (2000-08-15) claim 1 column 6, line 24 - line 26	12, 13, 16-21
	----- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

16 July 2004

Date of mailing of the international search report

27/07/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Rosenberger, J

INTERNATIONAL SEARCH REPORT

PCT/EP2004/004197

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	WO 2004/043863 A (MILLENNIUM INORGANIC CHEM) 27 May 2004 (2004-05-27) page 11, line 1 - line 4 -----	12, 13, 16-21

INTERNATIONAL SEARCH REPORT

PCT/EP2004/004197

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-11, 14, 15
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-11,14,15

Claim 1 defines seven process steps, which are executed in combination with the production steps of traditional ceramics. From the formulation of these steps it is apparent that it is impossible to execute all of these steps together within one single process, especially as it is unclear what the difference between the expressions ?covering glaze?, ?silk screening pastes?, ?engobe? and ?the layer covering? is. It is impossible to judge from independent claim 1 and also from the dependent claims 2-11 and from the description, which technical features are essential for the definition of the production process of the invention. Furthermore the process feature that ?the insufflation is designed to produce and improvement in the photocatalytic effect? is unclear, because it tries to define the invention by the result to be achieved, but it is not indicated how this result is achieved by adjusting specific parameters of the process.

Claim 14 and claim 15, which is dependent from claim 14, are also so unclear that a search for the subject-matter of this claim is impossible, because it is not indicated how the firing process is modified and which characteristics of the end product result from this modification.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 10018458	A	18-10-2001	DE 10018458 A1	18-10-2001
			WO 0179141 A1	25-10-2001
<hr/>				
JP 11157966	A	15-06-1999	NONE	
<hr/>				
US 6103363	A	15-08-2000	FR 2738813 A1	21-03-1997
			AT 210097 T	15-12-2001
			AU 7087596 A	01-04-1997
			BR 9610604 A	17-02-1999
			CZ 9800784 A3	12-08-1998
			DE 29624343 U1	29-05-2002
			DE 29624395 U1	16-01-2003
			DE 69617705 D1	17-01-2002
			DE 69617705 T2	08-08-2002
			DK 850204 T3	02-04-2002
			EP 1132351 A1	12-09-2001
			EP 0850204 A1	01-07-1998
			ES 2168506 T3	16-06-2002
			WO 9710186 A1	20-03-1997
			JP 11512337 T	26-10-1999
			PL 325527 A1	03-08-1998
			PT 850204 T	31-05-2002
			TR 9800459 T1	22-06-1998
			US 2002071956 A1	13-06-2002
			US 2002110638 A1	15-08-2002
			US 2002136934 A1	26-09-2002
			US 2002119307 A1	29-08-2002
			US 2002150681 A1	17-10-2002
			US 2003207028 A1	06-11-2003
			US 6326079 B1	04-12-2001
			US 2002028361 A1	07-03-2002
<hr/>				
WO 2004043863	A	27-05-2004	US 2004092393 A1	13-05-2004
			WO 2004043863 A1	27-05-2004
<hr/>				